

UNCLASSIFIED

AD NUMBER
ADC024160
NEW LIMITATION CHANGE
TO Approved for public release, distribution unlimited
FROM Distribution authorized to U.S. Gov't. agencies and their contractors; Specific authority; Dec 1980. Other requests shall be referred to Commander, Army Armament Research and Development Command, Attn: DRDAR-TSB, Aberdeen Proving Ground, MD 21005.
AUTHORITY
USARL ltr, 30 Oct 2002

THIS PAGE IS UNCLASSIFIED

UNCLASSIFIED

AD NUMBER

ADC024160

CLASSIFICATION CHANGES

TO: unclassified

FROM: confidential

LIMITATION CHANGES

TO:

Distribution authorized to U.S. Gov't. agencies and their contractors; Specific authority; Dec 1980. Other requests shall be referred to Commander, Army Armament Research and Development Command, Attn: DRDAR-TSB, Aberdeen Proving Ground, MD 21005.

FROM:

Distribution authorized to U.S. Gov't. agencies only; Test and evaluation; Dec 1980. Other requests shall be referred to Director, USA Ballistic Research Laboratory, Attn: DRDAR-TSB, Aberdeen Proving Ground, MD 21005.

AUTHORITY

31 Dec 1986, per document marking; AARDC, per DTIC Form 55

THIS PAGE IS UNCLASSIFIED

LEVEL
CONFIDENTIAL

AD-E420.568

2

COPY 14 OF 100 COPIES, SERIES A

AD

AD C024160

MEMORANDUM REPORT ARBRL-MR-03069

This Document
Reproduced From
Best Available Copy

A SURVEY OF THE THERMODYNAMICS OF
HAN-BASED LIQUID GUN PROPELLANTS (U)

Eli Freedman

December 1980

DTIC
ELECTE
FEB 24 1981
S D



US ARMY ARMAMENT RESEARCH AND DEVELOPMENT COMMAND
BALLISTIC RESEARCH LABORATORY
ABERDEEN PROVING GROUND, MARYLAND

Distribution limited to US Government agencies only; Test and
Evaluation; ~~Dec 80~~ Other requests for this document must be
referred to Director, USA Ballistic Research Laboratory,
ATTN: DRDAR-TSB, Aberdeen Proving Ground, Maryland 21005.

CLASSIFIED BY: NAVSEAINST 5511.62
dtd 28 Sep 1977

DECLASSIFY ON: 31 December 1986

NATIONAL SECURITY INFORMATION

*Unauthorized Disclosure Subject to Criminal
Sanctions*

81 0206 523

CONFIDENTIAL

CONFIDENTIAL

~~This page~~ is unclassified

When this report is no longer needed, Department of the Army organizations will destroy it in accordance with the procedures given in DOD 5200.1-R and AR 380-5. Navy and Air Force elements will destroy it in accordance with applicable directives. Department of Defense contractors will destroy the report according to the requirements of Section 14 of the Industrial Security Manual for Safeguarding Classified Information. All others will return the report to Director, US Army Ballistic Research Laboratory, ATTN: DRDAR-TSH, Aberdeen Proving Ground, Maryland 21005.

Secondary distribution of this report by originating or sponsoring activity is prohibited.

Additional copies of this report may be obtained from the Defense Technical Information Center, Cameron Station, Alexandria, Virginia 22314.

This document contains information affecting the national defense of the United States within the meaning of the Espionage Laws, Title 18 U.S.C. Sections 793 and 794. The transmission or the revelation of its contents in any manner to an unauthorized person is prohibited by law.

The findings in this report are not to be construed as an official Department of the Army position, unless so designated by other authorized documents.

The use of trade names or manufacturers' names in this report does not constitute endorsement of any commercial product.

CONFIDENTIAL

~~This page~~ is unclassified

(This page is unclassified)

UNCLASSIFIED

CONFIDENTIAL

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER MEMORANDUM REPORT ARBRL-MR-03069	2. GOVT ACCESSION NO. AD-20347606	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) A SURVEY OF THE THERMODYNAMICS OF HAN-BASED LIQUID GUN PROPELLANTS (U)	5. TYPE OF REPORT & PERIOD COVERED Final	
7. AUTHOR(s) Eli Freedman	6. PERFORMING ORG. REPORT NUMBER	
9. PERFORMING ORGANIZATION NAME AND ADDRESS US Army Ballistic Research Laboratory ATTN: DRDAR-BLI Aberdeen Proving Ground, MD 21005	8. CONTRACT OR GRANT NUMBER(s) 10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 1L161102AH43	
11. CONTROLLING OFFICE NAME AND ADDRESS US Army Armament Research & Development Command US Army Ballistic Research Laboratory (DRDAR-BL) Aberdeen Proving Ground, MD 21005	12. REPORT DATE DECEMBER 1980	
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)	13. NUMBER OF PAGES 26	
	15. SECURITY CLASS. (of this report) CONFIDENTIAL	
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE DECL: 31 Dec 86	
16. DISTRIBUTION STATEMENT (of this Report) Distribution limited to US Government agencies only; Test and Evaluation; Dec 1980. Other requests for this document must be referred to Director, US Army Ballistic Research Laboratory, ATTN: DRDAR-TSB, Aberdeen Proving Ground, Maryland 21005.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Liquid Propellants Thermodynamics Bipropellants Gun Propellant Hydroxylammonium Nitrate		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) (meg) (U) There are many reasons for thinking that the first liquid gun propellant to achieve type-classification will be a mixture of hydroxylammonium nitrate (HAN), water, and a miscible organic fuel. A survey has been made of the impetus pro- duced by such systems with more than twenty fuels. The results are found to depend strongly on the amount of water present in the mixture. The range of impetuses computed is surprisingly small, all of them lying within ten percent of either side of the mean. The ratio of oxidizer to fuel has only a slight		

DD FORM 1473
1 JAN 73

EDITION OF 1 NOV 65 IS OBSOLETE

UNCLASSIFIED

CONFIDENTIAL

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

(This page is unclassified)

UNCLASSIFIED

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE(When Data Entered)

20. Abstract (Cont'd):

effect on the results, although a flat maximum occurs on the fuel-rich side. The effect of non-ideal gas corrections on the results is noticeable, but still within the precision of available closed-bomb data. Significant advances in computations of this type require improved closed-bomb data.

Accession For	
NTIS GRA&I	<input type="checkbox"/>
DTIC TAB	<input checked="" type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By _____	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
B	

DTIC
ELECTE
FEB 24 1981
S D D

UNCLASSIFIED

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE(When Data Entered)

UNCLASSIFIED

(U) TABLE OF CONTENTS

	<u>Page</u>
LIST OF TABLES.	5
I. INTRODUCTION.	7
II. METHODOLOGY	7
III. RESULTS: THE EFFECT OF STRUCTURE	12
IV. RESULTS: EFFECT OF WATER	16
V. RESULTS: EFFECT OF OXIDIZER TO FUEL RATIO.	16
VI. RESULTS: BIPROPELLANTS	19
VII. DISCUSSION AND CONCLUSIONS.	19
ACKNOWLEDGMENTS	19
REFERENCES.	22
DISTRIBUTION LIST	23

The following page is blank.

UNCLASSIFIED

(U) LIST OF TABLES

<u>Table</u>		<u>Page</u>
1	Composition of Aqueous Monopropellants.	8
2	Enthalpies of Reaction for Organic Amines with Nitric Acid.	8
3	Summary of Thermodynamic Computations on HAN-Based Liquid Gun Propellants.	10
4	Effect of Chain Length on Computed Impetus.	15
5	Impetuses of Some HAN-Based Bipropellants	20

The following page is blank.

CONFIDENTIAL

I. (U) INTRODUCTION

(U) The search for acceptable liquid gun propellants (LGPs) has been going on for decades. Since most of the exposure of troops to LGPs will occur in training exercises, not in battle, the recent heightened awareness of the need for protection of personnel from toxic or corrosive materials has sharply reduced the variety of suitable materials for consideration. Thus, although hydrazine and some of its derivatives have shown good, even excellent, ballistic performance in tests, they must be regarded as unacceptable. Likewise, organic nitrates (e.g., propylene glycol dinitrate) are much too active physiologically to merit further consideration.

(C) These toxicological arguments are admittedly a posteriori, because a class of LGPs that have low vapor pressures and are non-corrosive has been known for some time. These LGPs contain hydroxylammonium nitrate (HAN) as an oxidizer, an organic fuel (a suitably chosen compound of C, H, O, and perhaps N), and water. Table 1 lists the compositions of some of these propellants. The most important member of this class is NOS-365, originally developed by the Navy¹ as a torpedo fuel to replace OTTO-II, which contains an organic nitrate.

(C) NOS-365 contains isopropylammonium nitrate (IPAN) as its fuel, and 20% by weight of water. (Henceforth, all percentages will be understood to be weight-percents, and will not be spelled out.) The HAN/IPAN mixture forms a subclass of HAN-based LGPs, each differing mainly in the percentage of water present.

(C) The ultimate test of any propellant, solid, liquid, or gas, is its behavior in a gun. Since gun firings are expensive, the more that can be learned by computer studies and small-scale laboratory testing, the better. The present paper is devoted entirely to thermodynamic computer studies. It has three aims: To see if IPAN is thermodynamically the best fuel; to consider the effect of the amount of water on computed performance; and to consider the effect of oxidizer to fuel ratio (O/F) on performance.

II. (U) METHODOLOGY

(U) The BLAKE² thermodynamics program was used throughout this work. Although it is slower than other codes, and has a comparatively limited library, it has the great advantage of being able to take into account

¹ (U) "Liquid Monopropellant Gun Exploratory Development Program," IHTR 405, 30 Aug 74 (Confidential report).

² (U) E. Freedman, "BLAKE -- A Thermochemical Code Based on TIGER," Paper 10 in "Proceedings of the International Symposium on Ballistics", Dover, NJ, 1973.

CONFIDENTIAL

CONFIDENTIAL

CONFIDENTIAL

TABLE 1. (U) COMPOSITION OF AQUEOUS MONOPROPELLANTS

<u>COMPONENT</u>	<u>NOS-283</u>		<u>NOS-365</u>		<u>NOS-411</u>	
	<u>WT %</u>	<u>MOBILITY</u>	<u>WT %</u>	<u>MOBILITY</u>	<u>WT %</u>	<u>MOBILITY</u>
HAN	56.9	8.08	60.7	8.83	64.5	9.47
IPAN	18.1	2.02	19.3	2.21	20.5	2.37
H ₂ O	25.0	18.90	20.0	15.50	15.0	11.80
Density						
(g/cm ³)	1.363		1.396		1.410	

CONFIDENTIAL

UNCLASSIFIED

TABLE 2. (U) ENTHALPIES OF REACTION FOR ORGANIC AMINES WITH NITRIC ACID

<u>AMINE</u>	<u>ΔH° (Reaction)</u> <u>joule per mole of amine</u>
Methylamine	-132.8
Ethylamine	-118.5
Trimethylamine	- 89.7
Triethylamine	-105.1
Dimethylamine	-114.8

UNCLASSIFIED

CONFIDENTIAL

CONFIDENTIAL

non-ideal gas effects. The code's application to LGPs containing HAN and water, while good, nevertheless leaves some room for improvement. The method for treating non-ideal gas effects in BLAKE applies strictly only to spherical nonpolar molecules, and is thus incorrect for water. This error is partially compensated by using appropriately adjusted values of the Lennard-Jones force constants from which the corrections for non-ideality are derived. In the case of LGPs where more than half of the product gases are water, the compensation is insufficient.

(U) The effect of this error is not so great as to invalidate either the comparisons made, or any of the conclusions reached.

(U) The code could readily be improved by incorporating the Stockmayer potential for water and ammonia, the two principal "offenders." But until closed-bomb values for LGPs are available, such a modification remains an unnecessary frill.

(U) A much more significant input parameter is the enthalpy of formation of the ingredients, and much effort was exerted to obtain the best available data in the literature. Wherever possible, data were taken from Cox and Pilcher's monumental compilation³. Some additional important values were located in Domalski's survey⁴.

(U) The only significant compounds for which data were lacking were some organic ammonium nitrates. Domalski⁴ gives enthalpies of formation for five of them, the salts of methyl, dimethyl, trimethyl, diethyl, and triethyl amines. Enthalpies of formation for all of the amines are in Cox and Pilcher³. Combining the data from these two sources, we get the enthalpies of reaction for the formation of the salts from their amines as shown in Table 2.

(C) The average enthalpy of reaction for these five salts is -112 ± 22 J. Excluding methylammonium nitrate changes the average to -107 ± 7 J. (This exclusion is reasonable because the first member of a homologous series often differs significantly from the higher members.) Ultimately, the value of -117 J, the value for ethyl, was chosen for both *n*-propyl and isopropyl ammonium nitrates, leading to the enthalpies of formation shown in Table 3.

(U) The enthalpy of formation of HAN used for all of these calculations was -366.5 J/mol⁵.

³(U) J.D. Cox and G. Pilcher, *"Thermochemistry of Organic and Organometallic Compounds"*, Academic Press, London, 1970.

⁴(U) E.S. Domalski, *J. Physical Chemical Ref. Data*, Vol. 1, p. 221, 1972.

⁵(U) *"Selected Values of Chemical Thermodynamic Properties"*, NBS Technical Note 270-3, 1968.

CONFIDENTIAL

CONFIDENTIAL

TABLE 3. (U) SUMMARY OF THERMODYNAMIC COMPUTATIONS ON HAN-BASED LIQUID GUN PROPELLANTS

(Water = 20% by Weight; Loading Density = 0.2 g/cm^3 ; L-J sigma = 10^{-6} m)

Fuel	C/H/N/O	$-\Delta H^\circ_f$ (J/mole)	O/F	I(J/g)	Notes
Ethyleneimine Nitrate	2/7/2/3	211.00	2.25	976.9	1
Trimethylammonium Nitrate (TMAN)	3/10/2/3	310.0	4.0	955.5	1
Tetramethylammonium Nitrate	4/12/2/3	344.0	5.5	950.4	1
Triethylammonium Nitrate	6/16/2/3	413.8	8.5	942.7	1
11-n-decylhenicosane	31/64/0/0	848.1	47.0	942.4	2
Tri-Octylammonium Nitrate	24/25/2/3	883.	35.5	942.2	1
Dimethylammonium Nitrate	2/8/2/3	346.9	2.5	937.1	3
Triethanolammonium Nitrate	6/16/2/6	728.	7.0	934.8	4
n-butylammonium Nitrate	4/12/2/3	431.	5.5	932.5	1
Isopropylammonium Nitrate (IPAN)	3/10/2/3	403.3	4.0	930.0	3
n-propylammonium Nitrate	3/10/2/3	404.6	4.0	929.7	3
2, 2-diethoxypropane	7/16/0/2	539.02	10.0	927.3	3
Dodecanoic Acid	12/26/0/2	774.58	17.5	925.4	2
Ethylammonium Nitrate	2/8/2/3	366.9	2.5	924.9	1
1, 4-dioxane	4/8/0/2	353.42	5.0	920.7	2
Tribenzylammonium Nitrate	18/16/2/3	155.	20.5	917.7	3
Pyridinium Nitrate	5/6/2/3	197.	5.0	916.6	3
Anilinium Nitrate	6/8/2/3	271.5	6.5	913.2	3
1, 3-dioxane	4/8/0/2	385.81	5.0	912.8	2
Methylammonium Nitrate	1/5/2/3	354.4	1.0	911.4	1
Ethylammonium Nitrate	2/8/2/4	517.1	2.0	897.8	4
8-hydroxyquinoline Nitrate	9/8/2/4	385.	9.0	895.3	3
Ethylenediammonium Nitrate	2/10/4/6	653.5	1.5	892.6	1
Ethylene Glycol	2/6/0/2	454.93	2.5	868.8	2
Triacetin	9/14/0/6	1331.	9.5	847.5	2
OTTO-II	-/-/-/-	---	---	866.7	-

Notes: 1 - ΔH°_f from Ref. 4.

3 - ΔH°_f for nitrate salt estimated by this writer.

2 - ΔH°_f from Ref. 3.

4 - ΔH°_f for both amine and its nitrate estimated by this writer.

CONFIDENTIAL

CONFIDENTIAL

(C) Another source of uncertainty in the enthalpy of formation data concerns the physical state of the individual ingredients in the final mixture. Propellant thermodynamic calculations are almost always made with the assumption that the enthalpy of formation of the final propellant is the sum of the enthalpies of formation of the ingredients, each weighted by its mole fractions. This procedure neglects all energies of interaction, and is a reasonable assumption for solid propellants. It may not be quite so reasonable for LGPs containing water, since heats of hydration are occasionally large. In the present case, the heat of solution of HAN is -22 J/mol for a 1 M solution⁵. The heat of solution decreases with increasing concentration; since NOS-365 contains 8.8 M HAN, it appeared that the value for the crystalline state was more appropriate than that for the solvate substance. (It is worth noting that in NOS-365 there are only two water molecules for each molecule of HAN.) The same assumption was made for all of the fuels, there being no data on heats of solution in any case. The necessary corrections can be made at once when more or better data become available, but the changes will not be significant.

(C) As will be shown later, the amount of water has a large effect on the results. This brings up a problem of a different sort. Most chemists working with solutions prefer to specify concentrations in molarities (i.e., the number of moles in 1000 cm^3 of solution), since they can then use volumes, which are readily and conveniently measured, to determine the amounts of reactants. Unfortunately, molarities change with density. Different fuels have different densities, and there is no general method known for computing the density of a solution from its ingredients other than by measurement after formulation. How then should the comparison between fuel A and fuel B be made? For example, NOS-365 can be specified in two different, although equivalent, ways either containing 60.70% HAN, 19.30% IPAN, and 20.00% water, or an containing 8.85 M HAN, 2.02 M IPAN, and 15.54 M water. Suppose one wants to compare the calculated performance of NOS-365 with that of a propellant containing a different fuel of the same empirical formula ($\text{C}_3\text{H}_{10}\text{N}_2\text{O}_3$), but with a density of 1.26 g/cm^3 (compared to 1.4 g/cm^3 for NOS-365). The percentage composition of this latter propellant is identical with that of NOS-365, but its molar composition is markedly different: 7.96 M HAN, 1.99 M fuel, and 13.99 M water. If this latter propellant is formulated to have the same molarities as NOS-365, then the percentage of water, for example, becomes 11.12%. This effect is evidently not trivial. In the belief that comparisons based on weight are more meaningful, they have been used consistently. This point should be considered an assumption, not a proven fact.

(U) All of the calculations were carried out uniformly for a loading density of 0.2 g/cm^3 . One of the advantages of LGPs is that they have high intrinsic densities, but there is no reason for making thermodynamic computations at such densities because shot start always occurs well before all-burnt. The effective loading density at shot start is likely to be greater than 0.2 g/cm^3 , but this number is a convenient

CONFIDENTIAL

CONFIDENTIAL

one for comparisons. It is large enough to show non-ideal gas effects, but not so large for them to have disproportionate effects on the results.

(U) The applications of LGPs in the field will likely be in volume-limited systems, which would make the volumetric impetus (impetus multiplied by density) the more useful quantity for comparison. Results obtained in this laboratory have shown that the densities of many HAN-based LPs can be estimated moderately well by assuming that specific volumes (the reciprocal of the densities) are additive. Thus, the density d , of a particular solution is

$$1/d = \sum w(i)/d(i)$$

where $w(i)$ is the weight fraction of component i , of density $d(i)$. This equation works well provided the quantities $d(i)$ for the individual components are chosen to fit some experimental points, rather than using handbook values. This is especially important for materials like HAN, which is a solid in its pure state. This additional step has not been included in the results reported here.

(U) To summarize: All of the results to be presented are for a specified weight-percent of water (usually 20%), for a specified oxidizer to fuel ratio (usually stoichiometric), and always for a loading density of 0.2 g/cm^3 .

III. (U) RESULTS: THE EFFECT OF STRUCTURE

(C) Table 3 presents the computed impetuses for 25 fuels, and also for OTTO-II. The most striking aspects of this table is how small the range of impetuses are. The distribution is plotted in Figure 1. Even though the fuels range from hydrocarbons to organic ammonium nitrates, from short chains to long chains and to rings, from aliphatic to aromatic to heterocyclic, the entire range of impetuses is only 847 to 977 J/g; the average value is 948. The dominant property determining the results is the enthalpy of formation, but the empirical formula does have some effect.

(C) The separation of the effect of the numbers of C, H, N, and O atoms on the calculated impetus from the effect of enthalpy is not obvious. An additional complication is the fact that the computations are carried out for stoichiometric mixtures with HAN. For a stoichiometric mixture of HAN ($\text{H}_4\text{N}_2\text{O}_4$) with a compound $\text{C}_x\text{H}_y\text{O}_z$ (the number of nitrogens is irrelevant), the ratio of oxidizer to fuel at stoichiometry is given by

$$\text{O/F} = x + (y/4) - (z/2)$$

UNCLASSIFIED

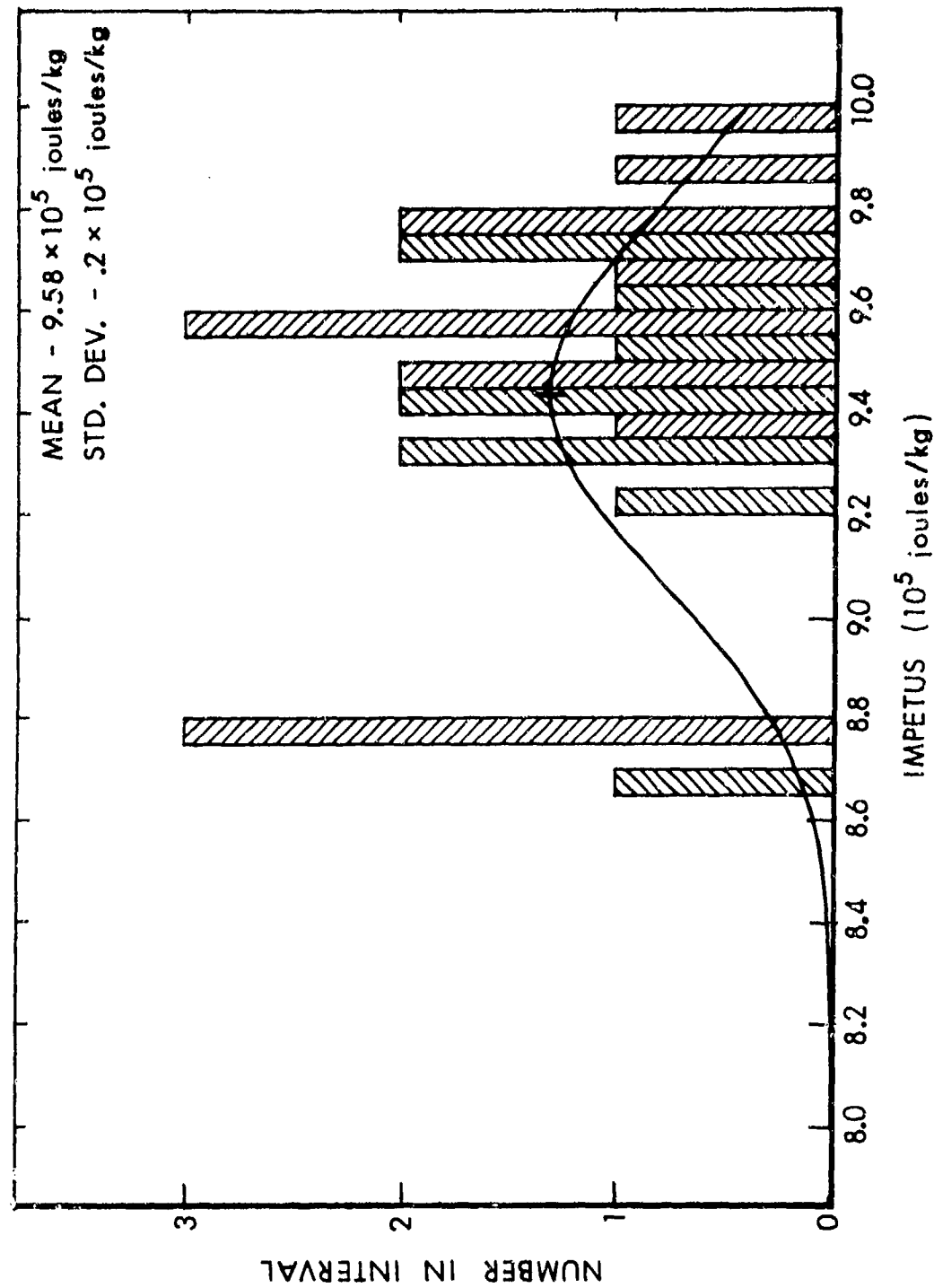


Figure 1. (U) Distribution of Computed Impetus of Liquid Propellants.

UNCLASSIFIED

CONFIDENTIAL

Changing x or y or z in general changes O/F (except for accidental cancellations). The overall result is a system with too many variables to permit the isolation of significant factors.

(U) M. Summerfield⁶ suggested that one way of looking for trends would be to consider the effects of a homologous series of the same family of compounds. For example, lengthening a carbon chain by adding one methylene group ($--CH_2--$) makes the enthalpy of formation about 21 J/mol more negative. Assuming that the enthalpy of formation of a C-4 ammonium nitrate is about -350 J/mol, one sees that the enthalpy of formation of an organic ammonium nitrate with n carbons is

$$\Delta H = -350 - 21(n-4)$$

For alcohols, the corresponding equation is

$$\Delta H = -305 - 21(n-4).$$

Table 4 shows the results of the calculation for the impetus as a function of n at stoichiometry and 20% water. The impetus increases with increasing chain length, but the rate of increase declines as the chain gets longer. The limiting value depends almost entirely on the fuel's enthalpy of formation, and hardly at all on its formula.

(C) We conclude that, based on all of the calculations performed up to now, the impetus of a liquid gun propellant composed of HAN in stoichiometric proportions with almost any fuel, and containing 20% by weight water, will fall in the range of 900 to 1000 J/g.

(U) This conclusion will not hold for molecules with sufficiently small negative enthalpies or positive enthalpies of any size. Empirically, however, it is known that such compounds are prone to decompose at or near ambient temperatures and thus, will not be suitable for LGPs. Likewise, fuels with exceptionally large negative enthalpies will have impetuses below 0.9 kJ/g, but such propellants are not likely to be useful.

(U) One additional assumption implicit in the foregoing calculations that has not been mentioned yet is that all of the listed compounds can be made.⁷ In fact, this is false for some of the listed organic ammonium nitrates. While there were some individual variations, attempts at synthesizing the organic ammonium nitrates with more than four carbons

⁶ (U) M. Summerfield, private communication, May 77.

⁷ (U) K.E. Travis, Interior Ballistics Division, BRL: Presentation given at the BRL Workshop on Liquid Propellants, May 77.

CONFIDENTIAL

CONFIDENTIAL

TABLE 4. (U) EFFECT OF CHAIN LENGTH ON COMPUTED IMPETUS

(Conditions the same as for Table 3)

<u>Class of Compound</u>	<u>No. of Carbons</u>	<u>$-\Delta H^{\circ}_f$ (J/mol)</u>	<u>Impetus (J/g)</u>
Organic Ammonium Nitrate	4	350	973.67
$C_n H_{2n+4} N_2 O_3$	6	392	973.73
	8	434	973.60
	10	476	973.76
Alcohol	4	305	956.65
$C_n H_{2n+2} O$	6	347	962.30
	8	389	965.16
	10	431	966.88
Hydroxy Acid	6	720	916.57
$C_n H_{2n+2} O_3$	7	753	923.88
	9	820	933.26
	11	895	938.32

CONFIDENTIAL

generally resulted in the amines being oxidized rather than nitrated. Tetramethylammonium nitrate was readily synthesized, but a mixture of it with HAN refused to burn on a hot plate, whereas NOS-365 reacts immediately in such a test.

IV. (U) RESULTS: EFFECT OF WATER

(C) In striking contrast to the weak dependence of impetus on the nature of the fuel is the strong dependence of the calculated impetus on the amount of water in the mixture. This effect is shown in Figure 2 for two formulations, NOS-365 and 1776. (Formulation 1776 is similar to NOS-365, except for the substitution of trimethylammonium nitrate for IPAN; also, the percentages are a trifle different for reasons explained elsewhere⁸).

(C) The effect of adding water is almost exactly linear: a one percent increase in the water content causes a one percent decrease in the impetus. This effect arises from the low molecular weight of water (18.015) compared to that of any other ingredient in the propellant. A change of one gram of water in a hundred grams of propellant (1%) of average molecular weight, 100 means a change of about 5.4% in the number of molecules in the propellant, accounting for the disproportionate effect of water. A similar, although less dramatic, effect has been noted in solid propellants.

V. (U) RESULTS: EFFECT OF OXIDIZER TO FUEL RATIO

(U) All of the calculations of the section entitled, "Results: The Effect of Structure", were made for stoichiometric mixtures; that is, the amount of HAN in the propellant was just sufficient to oxidize all of the carbon to carbon dioxide and all of the hydrogen to water. It has long been known that rocket fuels achieve maximum specific impulse of O/F ratios smaller than stoichiometric (i.e., fuel-rich); the same question naturally arises for LGPs.

(U) The answer turns out to be the same as for rocket propellants. This is shown in Figure 3. With LGPs, however, the effect is quite weak, so that there is no compelling reason to attempt to formulate LGPs at the precise maximum impetus. For any particular fuel, the actual O/F ratio, and the even more important matter of the amount of water in the formulation, will be determined not by the impetus, but by the burning characteristics of the propellant.

⁸ (U) E. Freedman and N. Travis, "Compositions, Nomenclature, and Densities of Aqueous Liquid Gun Propellants", Ballistic Research Laboratory Memorandum Report to be published.

CONFIDENTIAL

CONFIDENTIAL

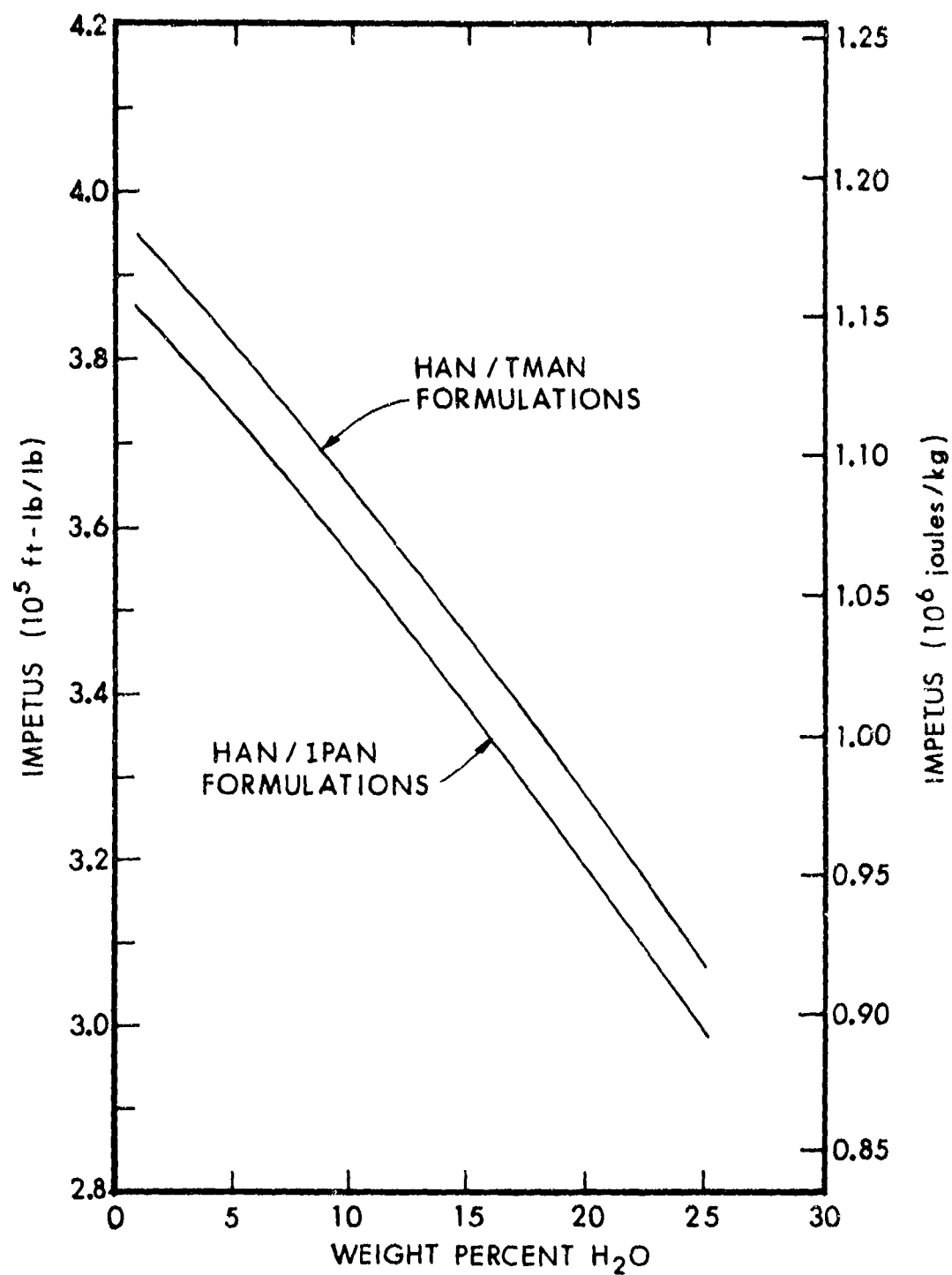


Figure 2. (U) Effect of H₂O on Impetus of Two Liquid Propellants.

CONFIDENTIAL

CONFIDENTIAL

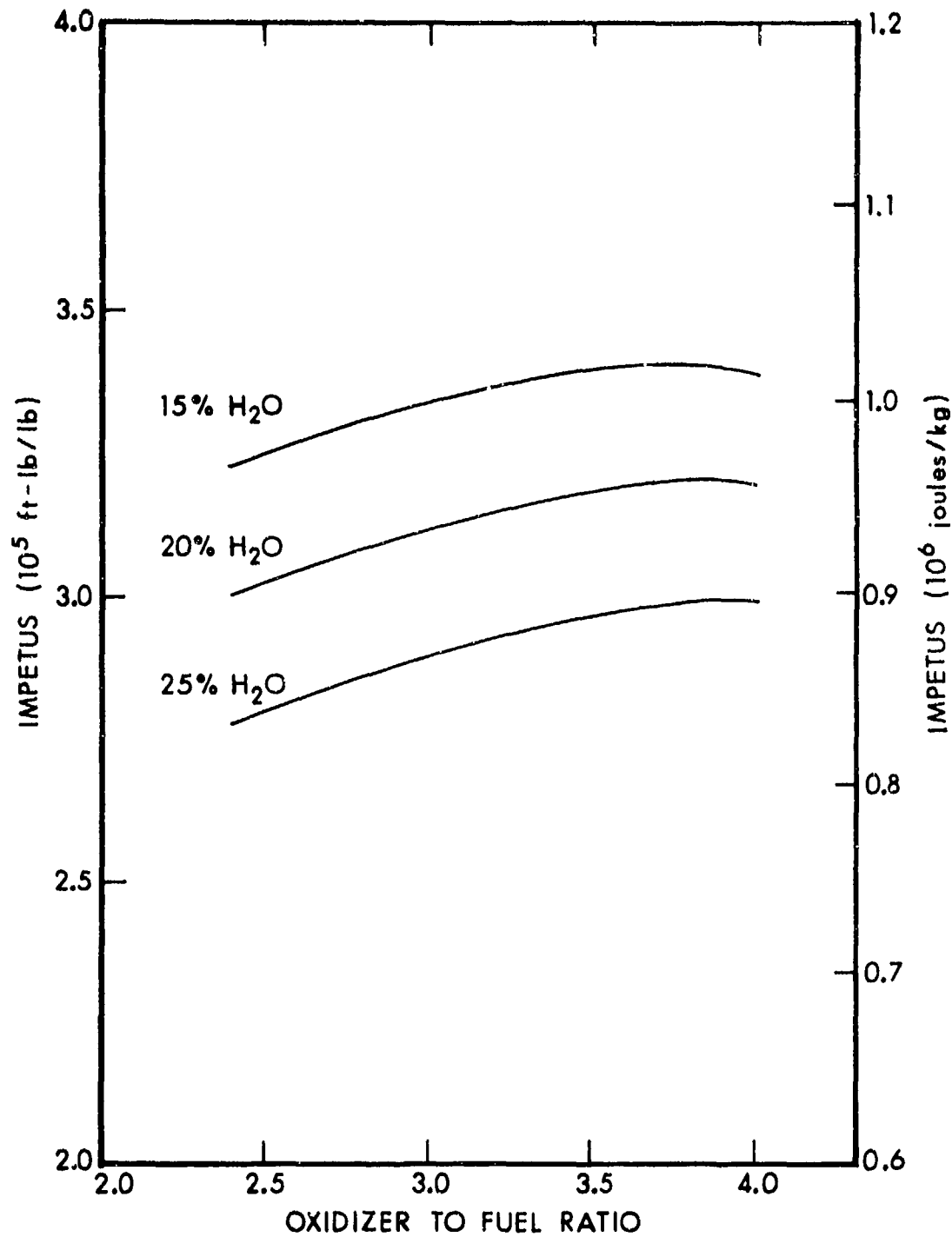


Figure 3. (U) Effect of Oxidizer/Fuel Ratio on Three Liquid Propellants.

CONFIDENTIAL

CONFIDENTIAL

VI. (U) RESULTS: BIPROPELLANTS

(U) BLAKE, in common with all other thermodynamic codes, assumes that all of the ingredients are mixed and burned homogeneously, regardless of the physical facts. (The discrepancy is especially noteworthy with solid small-arms propellants.) At first sight, then it might appear that bipropellants, whose components are immiscible with each other, could not be treated in the same way. Provided the combustion of the two components is complete, however, it is immaterial whether the initial starting materials were mixed or not. Table 5 summarizes calculations for a typical bipropellant, using decalin as the fuel and HAN as the oxidizer. Here, too, the strong dependence on the water content is noted. These results are shown graphically in Figure 4, where they are compared with NOS-365.

VII. (U) DISCUSSION AND CONCLUSIONS

(U) LP guns can be designed to use either monopropellants or bipropellants. Test firings in both bulk-loaded and regeneratively-injected LP guns have demonstrated high ballistic efficiencies. Regardless of which combination is used, thermodynamic calculations of the kind presented here will be generally valid, subject to assumptions already mentioned. Thus, the present results are not affected by the vigorous controversy that rages over the type of propellant, the gun design, and various other related matters.

(C) A glance at Table 3 shows that the class of HAN-based propellants does indeed offer considerable promise. Since the typical HAN-based propellant has a density of 1.2 g/cm^3 (or greater), these propellants possess even more spectacular volumetric impetuses.

(U) In conclusion: (1) the impetus of a HAN-based liquid gun propellant depends only weakly on the exact nature of the fuel; (2) it is a strong function of the amount of water present; (3) the impetus varies only weakly with the oxidizer to fuel ratio; (4) maximum impetus occurs with fuel-rich systems, but the effect is not worth consideration at this time; and (5) the volumetric impetus of HAN-based liquid propellants makes them even more attractive as LGP candidate systems.

(U) ACKNOWLEDGMENTS

(U) It is a pleasure to thank my colleagues, with whom all of the details of the report have been discussed at one time or another, especially Dr. Nathan Klein and Dr. Kenton E. Travis. Thanks are also due to Dr. Travis for his discussing with me his work on ingredient synthesis in advance of its publication. I also want to thank Mr. R.D. Anderson (Ignition and Combustion Branch) for advice on the UNIVAC, and Dr. Walter F. Morrison for technical assistance.

CONFIDENTIAL

UNCLASSIFIED

TABLE 5. (U) IMPETUSES OF SOME HAN-BASED BIPROPELLANTS

<u>Fuel</u>	<u>O/F</u>	<u>Water (%)</u>	<u>Impetus (J/g)</u>
Decalin	12/1	1	1187.5
Decalin	12/1	5	1142.4
Decalin	12/1	15	1019.6
Decalin	14/1	20	969.0

UNCLASSIFIED

CONFIDENTIAL

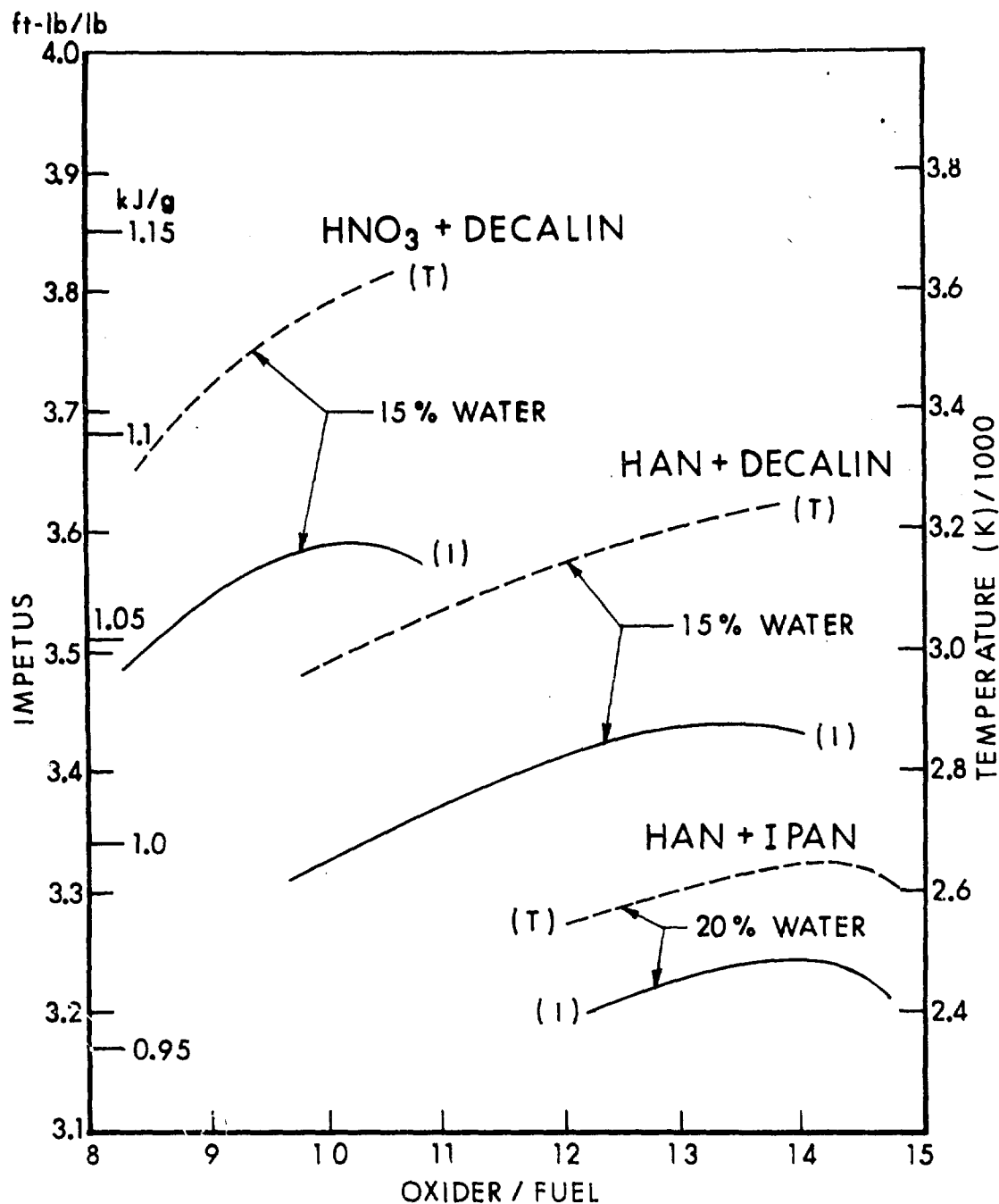


Figure 4. (U) Effect of Oxidizer/Fuel Ratio on Two Liquid Bipropellants.

CONFIDENTIAL

UNCLASSIFIED

(U) REFERENCES

1. "Liquid Monopropellant Gun Exploratory Development Program", IHTR 405, 30 Aug 74 (Confidential report).
2. E. Freedman, "BLAKE -- A Thermochemical Code Based on TIGER", Paper 10 in "Proceedings of the International Symposium on Ballistics", Dover, NJ, 1973.
3. J.D. Cox and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds", Academic Press, London, 1970.
4. E.S. Domalski, J. Physical Chemical Ref. Data, Vol. 1, p. 221, 1972.
5. "Selected Values of Chemical Thermodynamic Properties", NBS Technical Note 270-3, 1968.
6. M. Summerfield, private communication, May 77.
7. K.E. Travis, Interior Ballistics Division, BRL: Presentation given at the BRL Workshop on Liquid Propellants, May 77.
8. E. Freedman and K. Travis, "Compositions, Nomenclature, and Densities of Aqueous Liquid Gun Propellants", Ballistic Research Laboratory Memorandum Report to be published.

UNCLASSIFIED

(U) DISTRIBUTION LIST

<u>No. of Copies</u>	<u>Organization</u>	<u>No. of Copies</u>	<u>Organization</u>
2	Commander Defense Technical Info Center ATTN: DDC-DDA Cameron Station Alexandria, VA 22314	3	Commander US Army Armament Research and Development Command Benet Weapons Laboratory ATTN: DRDAR-LCB-TL R. Hasenbein P. Votis Watervliet, NY 12189
1	Director Defense Advanced Research Projects Agency ATTN: LTC C. Buck 1400 Wilson Boulevard Arlington, VA 22209	1	Commander US Army Armament Materiel Readiness Command ATTN: DRSAR-LEP-L, Tech Lib Rock Island, IL 61299
1	HQDA (DAMA, C. Church) Washington, DC 20310	1	Commander US Army Aviation Research and Development Command ATTN: DRSAR-E 12th and Spruce Streets St. Louis, MO 63166
1	Commander US Army Materiel Development and Readiness Command ATTN: DRCDMD-ST 5001 Eisenhower Avenue Alexandria, VA 22333	1	Director US Army Air Mobility Research and Development Laboratory Ames Research Center Moffett Field, CA 94035
5	Commander US Army Armament Research and Development Command ATTN: DRDAR-TSS (2) H. Fair, DRDAR-LC J.P. Picard, DRDAR-LC D. Downs, DRDAR-LC Dover, NJ 07801	1	Commander US Army Communications Research and Development Command ATTN: DRDCO-PPA-SA Fort Monmouth, NJ 07703
5	Commander US Army Armament Research and Development Command ATTN: W.L. Quine, DRDAR-LC A.J. Beardell, DRDAR-LC J. Hershkowitz, DRDAR-LC N. Slagg, DRDAR-LC M. Devine, DRDAR-SC Dover, NJ 07801	1	Commander US Army Electronics Research and Development Command Technical Support Activity ATTN: DELSD-L Fort Monmouth, NJ 07703
		1	Commander US Army Harry Diamond Labs ATTN: DRXDO-TI 2800 Powder Mill Road Adelphi, MD 20783

UNCLASSIFIED

UNCLASSIFIED

(U) DISTRIBUTION LIST

<u>No. of</u> <u>Copies</u>	<u>Organization</u>	<u>No. of</u> <u>Copies</u>	<u>Organization</u>
2	Commander US Army Missile Command ATTN: DRSMI-R DRSMI-YDL Redstone Arsenal, AL 35809	2	Commander Naval Surface Weapons Center ATTN: O. Dengel K. Thorsted Silver Spring, MD 20910
2	Commander US Army Mobility Equipment Research and Development Cmd ATTN: DRDME-WC DRSME-RZT Fort Belvoir, VA 22060	3	Commander Naval Weapons Center ATTN: S. Wood L. Liedtke China Lake, CA 93555
1	Commander US Army Tank Automotive Research and Development Cmd ATTN: DRDTA-UL Warren, MI 48090	1	Commander Naval Ordnance Laboratory ATTN: K. Mueller Indian Head, MD 20640
1	Director US Army TRADOC Systems Analysis Activity ATTN: ATAA-SAL White Sands Missile Range NM 88002	1	Superintendent Naval Postgraduate School ATTN: T. Houlihan Monterey, CA 93940
1	Office of the Chief of Naval Operations ATTN: Code NOP-351G Washington, DC 20360	1	Commander Naval Ordnance Station ATTN: G. Poudrier Indian Head, MD 20640
2	Commander Naval Sea Systems Command ATTN: SEA-55GH SEA-62R2, J. Murrin Washington, DC 20360	1	AFOSR/NA, L. Caveny Bldg 410 Bolling AFB, DC 20332
2	Commander Naval Surface Weapons Center ATTN: W.C. Wieland T. Tschirn Dahlgren, VA 22448	2	AFATL/ATWG, O. Heiney DLD, D. Davis Eglin AFB, FL 32542
		2	US Bureau of Mines ATTN: R.A. Watson 4800 Forbes Street Pittsburgh, PA 15213
		1	Director Los Alamos Scientific Laboratory ATTN: D. Butler P.O. Box 1663 Los Alamos, NM 87545

UNCLASSIFIED

UNCLASSIFIED

(U) DISTRIBUTION LIST

<u>No. of Copies</u>	<u>Organization</u>	<u>No. of Copies</u>	<u>Organization</u>
1	Director Jet Propulsion Laboratory ATTN: Tech Lib 4800 Oak Grove Drive Pasadena, CA 91103	1	Mechanical Technology, Inc. ATTN: A. Graham 968 Albany-Shakes Road Lathan, NY 12110
2	Director National Aeronautics and Space Administration ATTN: MS-603, Tech Lib MS-86, Dr. Povinelli 21000 Brookpark Road Lewis Research Center Cleveland, OH 44135	1	Pulsepower Systems, Inc. ATTN: L.C. Elmore 815 American Street San Carlos, CA 93555
1	Director National Aeronautics and Space Administration Manned Spacecraft Center Houston, TX 77058	1	AFELM, The Rand Corporation ATTN: Library-D 1700 Main Street Santa Monica, CA 90406
1	Calspan Corporation ATTN: E. Fisher P.O. Box 400 Buffalo, NY 14221	1	Science Applications, Inc. ATTN: R. Edelman 20335 Ventura Blvd Woodland Hills, CA 91364
1	Food & Machinery Corporation Northern Ordnance Division ATTN: J. Oberg Columbia Heights Post Office Minneapolis, MN MN 55421	1	Shock Hydrodynamics ATTN: W. Anderson 4710-16 Vineland Avenue N. Hollywood, CA 91602
4	General Electric Ordnance Dpt ATTN: J. Haskins J. Mandzy R.E. Mayer H. West 100 Plastics Avenue Pittsfield, MA 01201	1	TRW Systems ATTN: RL-1032, E. Fishman 1 Space Park Redondo Beach, CA 90278
2	General Electric Company Armament Systems Department ATTN: E. Ashley M. Bulman Burlington, VT 05401	1	Director Applied Physics Laboratory The Johns Hopkins University Johns Hopkins Road Laurel, MD 20810
		2	Director Chemical Propulsion Information Agency The Johns Hopkins University ATTN: T. Christian Tech Lib Johns Hopkins Road Laurel, MD 20810

CONFIDENTIAL
(This page is unclassified)

UNCLASSIFIED

DISTRIBUTION LIST

<u>No. of Copies</u>	<u>Organization</u>
1	Pennsylvania State University Applied Research Laboratory ATTN: K. Kuo University Park, PA 16802
1	Princeton University Department of Aerospace and Mechanical Sciences ATTN: Tech Lib James Forrestal Campus Princeton, NJ 08540
1	SRI International ATTN: Code L3106, G.A. Branch 333 Ravenswood Avenue Menlo Park, CA 94025
1	University of Mississippi Mechanical Engineering Dept. ATTN: C. R. Wimberly University, MS 38677

Aberdeen Proving Ground

Dir, USAMSAA
ATTN: DRXSY-D
DRXSY-MP, H. Cohen
Cdr, USATECOM
ATTN: DRSTE-TO-F
Dir, USACSL, Bldg. E3516
ATTN: DRDAR-CLB-PA

CONFIDENTIAL
(This page is unclassified)

UNCLASSIFIED

UNCLASSIFIED

USER EVALUATION OF REPORT

Please take a few minutes to answer the questions below; tear out this sheet and return it to Director, US Army Ballistic Research Laboratory, ARRADCOM, ATTN: DRDAR-TSB, Aberdeen Proving Ground, Maryland 21005. Your comments will provide us with information for improving future reports.

1. BRL Report Number _____
2. Does this report satisfy a need? (Comment on purpose, related project, or other area of interest for which report will be used.)

3. How, specifically, is the report being used? (Information source, design data or procedure, management procedure, source of ideas, etc.) _____

4. Has the information in this report led to any quantitative savings as far as man-hours/contract dollars saved, operating costs avoided, efficiencies achieved, etc.? If so, please elaborate.

5. General Comments (Indicate what you think should be changed to make this report and future reports of this type more responsive to your needs, more usable, improve readability, etc.) _____

6. If you would like to be contacted by the personnel who prepared this report to raise specific questions or discuss the topic, please fill in the following information.

Name: _____

Telephone Number: _____

Organization Address: _____

UNCLASSIFIED



DEPARTMENT OF THE ARMY
UNITED STATES ARMY RESEARCH LABORATORY
ABERDEEN PROVING GROUND MD 21005-5066



REPLY TO
THE ATTENTION OF

AMSRL-CS-IO-SC (380)

30 OCT 2002

MEMORANDUM FOR SEE DISTRIBUTION

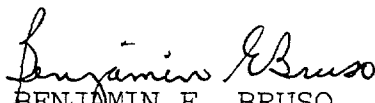
SUBJECT: Distribution Statement for U.S. Army Ballistic Research
Laboratory Memorandum Report ARBRL-MR-03069

1. Reference: U.S. Army Ballistic Research Laboratory
Memorandum Report ARBRL-MR-03069, "A Survey of the Thermodynamics
of HAN-Based Liquid Gun Propellants", E. Freedman, December
1980, UNCLASSIFIED.

2. Subject area experts and release authorities have reviewed
the referenced report and have determined that the report's
distribution statement may be cancelled. Request that you mark
your copy of the report:

APPROVED FOR PUBLIC RELEASE; DISTRIBUTION IS UNLIMITED

3. Our action officer is Mr. Douglas J. Kingsley, telephone
410-278-6960.


BENJAMIN E. BRUSO
Team Leader, Security/CI Office